

Technical Memorandum No. 33-254

*Review of Solid Propellants
for Space Exploration*

Frank J. Hendel

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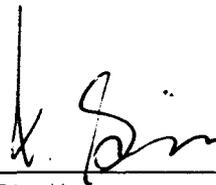
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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W. Gin, Manager

Solid Propellant Engineering Section

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ABSTRACT

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Various families of solid propellants which are or could be used in space vehicles and spacecraft are reviewed. These include polyurethane, polybutadiene-acrylic acid, polybutadiene-acrylic acid-acrylonitrile, carboxyl-terminated polybutadiene, double base, and thermoplastic polymers as fuel and binders of the crystalline oxidizers with or without aluminum or beryllium powder. Future solid propellants will have improved physical properties and specific impulse. Improved specific impulse will result from the use of energetic oxidizers, such as lithium ozonide, energetic fuel-binders such as nitro-polymers and acetylenic polymers, and energetic fuel ingredients such as light metal hydrides. An ultra-energetic cryogenic solid propellant could be made by freezing a mixture of liquid oxygen and hydrogen or a light metal hydride. A "cold" solid propellant made from BeH_2 and frozen hydrogen peroxide will have a theoretical vacuum specific impulse of almost 500 sec.

I. INTRODUCTION

Solid propellant rockets are being used in the exploration of space by instrumented or manned spacecraft injected as satellites into Earth orbits, by sounding rockets, and by lunar and planetary probes. Many of the launch vehicles are also using solid rockets. Because of the simplicity and intrinsic higher reliability, particularly during dynamic and/or weightless conditions, solid rockets will continue to be used in future space explorations.

Although all-solid propellant launch vehicles are preferred for missiles (because of their smaller size and instantaneous readiness), only moderate use of them is made on current space vehicles. The *Scout*, a launch vehicle for many international spacecraft and near-space experiments, as well as many research rockets, use solid propellant motors for launch. However, very large solid

propellant boosters (10 to 13 ft in diameter) have already been tested and will be used for launching spacecraft with or without liquid engines (as in the case of *Titan III-C*). Preparations are underway to develop solid motors which will be 20 ft in diameter and have a thrust of several million pounds. These very large motors (Refs. 1 and 2) may eventually replace the liquid propellant boosters presently used on the *Saturn I-B* and contemplated for use in the *Saturn V* launch vehicles.

A large liquid propellant launch vehicle usually depends on auxiliary solid propellant motors for stage separation (retro or posigrade rockets), for achieving the proper net-positive-suction-head prior to start of the second and upper stages (ullage rockets), and for many ordnance devices where solid propellant is required for generating

hot compressed gas. Solid propellant may also be used for tank pressurization, turbopump starters, attitude controls, and auxiliary power systems.

The safety of the astronauts during launch is heavily dependent on the launch escape systems which must be instantaneously ready for firing and the development of adequate thrust. The *Mercury* launch escape system consisted of two solid propellant motors, while the one to be used for *Apollo* will consist of three motors arranged in tandem. The *Gemini* Project relies on ejection seats which use solid propellant motors. Future spacecraft and space stations will use a combination of ejection seat and pressurized capsule or an escape system for the astronaut either on the launch pad, during the ascent trajectory, or from a spacecraft or space station already in space. Such devices will also use solid propellant motors for ejection.

Many past and present launch vehicles for unmanned spacecraft have been using either a single or a cluster of solid propellant motors for their upper stages. The present solid propellant motors do not have the restart capability of the liquid propellant engines used on the upper stages. However, recent developments proved the feasibility of several restarts of solid propellant motors (wafer technique, water quench, chamber pressure modulation, etc.). The latter development, coupled with a "dual-thrust" system (a unique characteristic of certain solid rockets), may replace liquid or hybrid propellant engines in upper stages.

Spacecraft orbital changes (in case of *Syncom* and *Early Bird* from elliptical to circular) have in the past been accomplished with solid propellant motors. Fairly large

solid motors are now being developed for future applications for this purpose. Retrograde and posigrade rockets for spacecraft use either solid or liquid propellant engines or both. The landing of the *Surveyor* spacecraft on the lunar surface will be effected, in part, by means of a solid propellant retro-rocket, while the *Apollo* Lunar Excursion Module (LEM) will use liquid propellant retro-rockets for lunar landing.

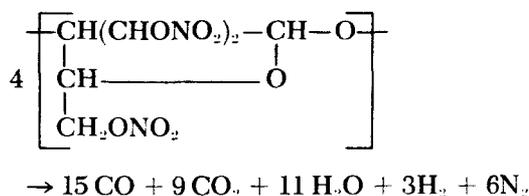
Unlike the liquid propellant systems, which usually use commercially available chemicals, solid propellant systems require special mixtures of many chemicals in a polymeric matrix. Because of the complexity of these mixtures and special processing techniques required, the solid grains are manufactured only by certain solid rocket plants and not by the usual chemical manufacturers. Within the last two decades, solid-propellant technology has made significant advances by achieving a higher specific impulse, higher propellant density, improved physical and mechanical properties (moisture resistance, lack of resonant or unstable burning), and better manufacturing methods and equipment including continuous mixing. At the same time, the application of cast and case-bonded propellant grains greatly reduced the weight of the previously thick heavy liners, eliminated restrictions, and avoided the cumbersome problem of suspension and "trapping" of the free-standing grain.

During the last 10 to 15 yr, the primary effort in solid-propellant technology consisted of developing improved polymeric binder-fuel, and more recently in research of techniques to incorporate high-energy solid oxidizers and fuels in the solid propellant. While the latter effort thus far has had limited success, the former effort produced a series of excellent polymeric binder fuels.

II. DOUBLE-BASE PROPELLANTS

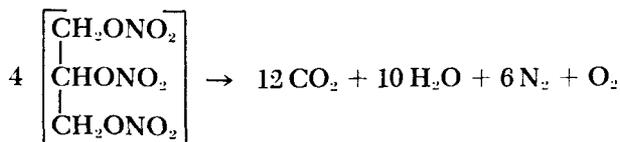
These propellants are almost fully homogeneous, and hence belong to the class of homogeneous or colloidal propellants where the oxidizer and the fuel are present in a single phase. The main ingredients of the double-base propellants are nitrocellulose and nitroglycerine. Nitrocellulose or cellulose nitrate is an ester obtained by reacting purified cotton linters with a mixture of nitric and sulfuric acids. The chief types of nitrocellulose which are used in solid propellants are: (1) soluble pyroxyline (collodion cotton, or dynamite cotton), containing 11.5 to 12.3% nitrogen and (2) guncotton, containing 12.5 to 13.5% nitrogen. Both are mixtures of di- and tri-nitrates of cellulose. There is a third type of nitrocellulose called celluloid pyroxyline which, however, contains only 10.5 to 11% nitrogen, and hence, being a low-energy compound, is not used in propellant work.

The equation for the decomposition of cellulose trinitrate (which contains 14.5% nitrogen) into products cooled to 2000°F may be written as:

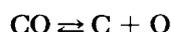
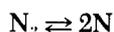
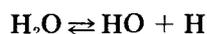
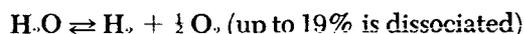
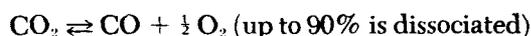


Thus, it is evident that even the trinitrate is highly underoxidized in its molecule. Nitrocellulose has been used as a "single-base propellant" but only to a limited extent. A mixture of nitrocellulose with nitroglycerine results in a higher energy propellant not only because nitroglycerine is a high-energy compound, but because its molecule is also overoxidized, thus helping in the oxidation of nitrocellulose.

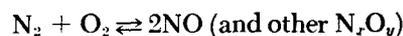
Nitroglycerine or glyceryl nitrate is made by reaction of glycerol with nitric acid in the presence of sulfuric acid. It is an oil which freezes at 13°C. The decomposition reaction into products cooled to 2000°F may be written as follows:



Owing to the elevated temperature in rocket combustion chamber, the products of nitrocellulose and nitroglycerine decomposition are dissociated to a great extent as follows (but are mostly recombined in the exhaust):



The following secondary reactions also take place at high temperatures:



Nitroglycerine is both an oxidizer and a high-energy plasticizer for the solid nitrocellulose. Stabilizers such as diphenylamine (which is also a nonexplosive plasticizer) and/or ethyl centralite (symmetrical diethyldiphenylurea) are added to reduce the rate of spontaneous decomposition, i.e., to desensitize the nitrocellulose and nitroglycerine mixture. Other additives (Table 1 and Refs. 3 and 4) in small quantities include potassium sulfate as a flash suppressor and carbon black as an opacifying agent (i.e., to prevent the radiative heat from reaching the layers of propellant closest to the burning surface). The double-base propellant ingredients are also mixed with ammonium perchlorate and aluminum powder to form higher performance *double-base composite* propellants (Ref. 5). In these formulations the sensitive nitroglycerine is often substituted by more stable, but less energetic, plasticizers such as trimethylolethane trinitrate.

Large grains are manufactured by the "ball process." The nitrocellulose is dissolved in a solvent such as ethylacetate and mixed with solid additives. The solvent is then evaporated and the solid product granulated. The granules are then placed in the rocket chamber which, after evacuation, receives the liquid plasticizer (between 10 and 50% of the total grain); the plasticizer fills the evacuated interstices and, after several days of "curing" at approximately 110°F, the whole mass coalesces into a solid grain. Another process, also widely used, mixes all

the ingredients into a slurry which is subsequently cast into the rocket chamber. This is the *plastisol*¹ or *nitroplastisol* process (Ref. 6). If the grain is not properly prepared and cured, the liquid plasticizer (nitroglycerine) may ooze out (*exude*) in hot weather or in flight, resulting in rapid deterioration.

The inherent safety problems associated with double-base propellants have stimulated considerable research and development in advanced manufacturing processes. One such process uses an inert carrier, either a liquid of a fairly low boiling point or a gas (Ref. 7). The carrier desensitizes the various ingredients during the mixing stage. Since neither the liquid nor the gas carrier dissolves to any appreciable extent in the propellant ingredients, it is fairly easy to separate the carrier from the mixture before or during the casting phase. Usually decanting and vacuum are sufficient to achieve good final results. Double-base (and also composite) propellants prepared by the above method closely approach both the physical and ballistic properties of formulations prepared by the conventional methods.

Part of the nitrocellulose may also be substituted by other highly nitrated solid polymers and even by ammonium perchlorate. As the amount of ammonium perchlorate in these formulations is relatively small, the

¹In general *plastisol propellants* use a thermoplastic polymer which requires a plasticizer. The plasticizer and the polymer dissolve in each other like nitroglycerine and nitrocellulose at 110°F or like polyvinyl chloride (PVC) and dioctyl phthalate (a plasticizer) at about 300°F. The latter mixture was used for many years for *plastisol composite propellants*. Volatile organic solvents may be added for ease in mixing and later evaporated to make *organisol (organosol) propellants*.

impact sensitivity is still high (20 to 30 kg-cm); hence, these propellants still belong to the Class A or 9² group of explosives. Handling, processing, transporting, and storing of such propellants require precautions (including table of quantity distances) for highly sensitive materials.

Another disadvantage of the double-base propellants is the fairly narrow temperature range in which they can be used (-10 to 130°F). Very often the good performance of double-base propellant rockets is offset by the weight of additional insulation or the requirement for heating them in space applications.

²Class 9 and Class 2 are ordnance classifications; these classes encompass propellants which correspond to double-base and single-base explosives (or propellants) respectively. Code of federal regulations (CFR) uses a different classification for transportation: Class A, Type 9, 8, 7, etc., Class B, and Class C refer to explosives (or propellants) in order of their decreased hazard.

Table 1. Typical double-base propellant (JP-N)^a (Ref. 4)

Material	Weight percent	Purpose
Nitrocellulose (13.25% N)	51.40	Polymer
Nitroglycerin	42.93	Explosive plasticizer
Diethyl phthalate	3.20	Nonexplosive plasticizer
Ethyl centralite	1.00	Stabilizer
Potassium sulfate	1.20	Flash suppressor
Carbon black	0.20	Opacifying agent
Candelilla wax	0.07	Die lubricant
Total	100.00	

^aThe flame temperature of this propellant in a rocket operating at constant pressure is 5,300°F.

III. COMPOSITE PROPELLANTS

Most of these propellants, being less sensitive than the double-base propellants, belong to the Class B (CFR) or Class 2 (Army Ordnance) group of explosives. Composite propellants are mixtures of ground, solid oxidizer with or without powdered light metals (or their solid hydrides) in a matrix of plastic, resinous or elastomeric binder which must be liquid or semi-liquid during mixing. The matrix provides the binder for the embedded solids while serving at the same time as fuel. Powdered light metals or their solid hydrides serve as medium- or high-energy fuel. All solid ingredients should be ground in such a way that the smaller particles can fill the interstices formed by the larger particles.³ Such combination requires a minimum amount of binder, while still retaining the good physical properties of the propellant. Usually a minimum amount of the binder results in the highest specific impulse (or performance) of the propellant. The addition of light metals or their hydrides produces a higher theoretical specific impulse. On the other hand, the combustion of these ingredients results in some loss of efficiency due to the "two-phase flow." This phenomenon is caused by solid or liquid particles of condensed species exhausted through the nozzle.

Composite propellants are often referred to as heterogeneous propellants in contrast to propellants discussed in the previous section. The early composite propellants were: (1) black powder consisting of potassium nitrate, charcoal, and sulfur serving as binder and fuel;

³Maximum sedimentation volume (Φ_{max}), which is the maximum packing of the solid particles, is an important parameter to achieve the highest possible solid loading in the propellant grain by reducing the interparticle volume (Private communication by B. G. Moser and Ray Wiech of the Jet Propulsion Laboratory).

(2) asphalt propellant consisting of potassium perchlorate, refinery asphalt, and hydrocarbon oil; and (3) early polymeric propellants comprising either a thermoplastic or thermosetting (curing) polymer as binder-fuel. The polymers which were, and sometimes are still, in use consist of phenolic resins, polystyrene usually as a copolymer with methyl methacrylate, polycsters, urea-aldehydes, cellulose, ethyl cellulose, nitrocellulose, epoxy resins, vinyl polymers such as polyvinyl chloride and polyvinyl acetate, polysulfide polymer, and gum stocks such as neoprene (GR-M), styrene-butadiene rubber (SBR previously called GR-S), and butyl rubber (GR-I). The gum stocks have to be masticated by a rubber mill or an intensive mixer, such as the Banbury, in order to incorporate the solid oxidizer into them. Table 2 shows typical formulations of composite propellants.

A. Polyurethane (or Polyurethan) Propellant

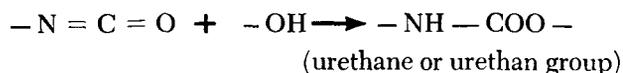
From 1954 until recently, this thermosetting propellant was the most important solid propellant for rocket application (Ref. 5). Its chief drawbacks are a tendency to crystallize at low temperature and a sensitivity to moisture in processing and in storage. Over a number of years, many improvements have been made in polyurethane propellants by the introduction of certain chemically active additives to reduce this drawback. One of the additives is absorbed on the surface of the oxidizer and forms a hard membrane linked to the polyurethane binder through a formation of a polyurethane bond.

The polyurethane binder is a homopolymer formed in a chemical reaction (during curing) of a high molecular weight glycol, preferably having hydroxyl groups at both

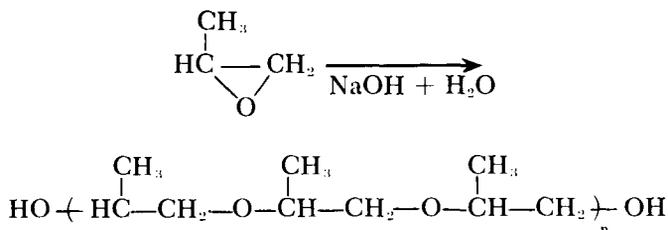
Table 2. Typical composite propellants (Ref. 4), wt %

Polysulfide		Vinylpolyester			Rubber			Polyurethane			Polybutadiene copolymer	
NH ₄ ClO ₄	71.00	NH ₄ NO ₃		72.50	NH ₄ NO ₃		86.50	KClO ₄		12.00	NH ₄ ClO ₄	68.00
Binder	26.00	NH ₄ ClO ₄	64.60		NH ₄ ClO ₄	90.00		NH ₄ ClO ₄	62.00	70.00	Aluminum	16.00
Catalysts	2.00	KClO ₄	11.40		Binder	7.00	11.30	Binder	21.40	17.50	Binder	16.00
Additives	1.00	Binder	23.60	25.50	Plasticizer	2.90		Aluminum	15.50			
		Catalysts	0.25		Catalyst	0.10	2.20	Additives	1.10	0.50		
		Additives	0.15	2.00								
Total	100.00	Total	100.00									

ends of the linear chain (alpha-omega termination) with a diisocyanate forming a urethane linked polymer:

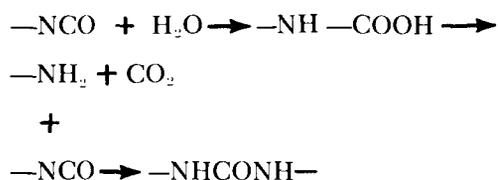


Poly(oxypropylene) glycol of 1,000 to 2,000 molecular weight is made by polymerizing usually propylene oxide (using aqueous NaOH as the catalyst and propylene glycol as the initiator) (Ref. 8):



The high-molecular-weight glycol is a difunctional¹ hydroxyl-terminated polypropylene oxide where R—O— at both ends forms R—OH with water. The vernacular name, polypropylene glycol (PPG), often given to this prepolymer is slowly disappearing.

The diisocyanate compound is usually 2, 4-toluene (or toluene) diisocyanate (TDI) which is used in a slight excess of the stoichiometric or equivalent ratio (—NCO)/(—OH). The excess (around 5%) is necessary to remove the traces of moisture² from all the ingredients of the propellant mixture. The excess of TDI reacts with H₂O forming CO₂ which is removed by mixing under vacuum, while the amino group formed links the chains (similar to the —OH group):



The third building block in the polyurethane polymer is a triol (such as hexane triol), which causes cross-linking of the linear polymeric chains. The amount of the triol should be fairly low (usually about 1/2% of the polymeric diol) in order to prevent an excessive cross-link density which results in a decreased elongation of the grain. On the other hand, too low a concentration of the cross-linking agent results not only in reduced tensile

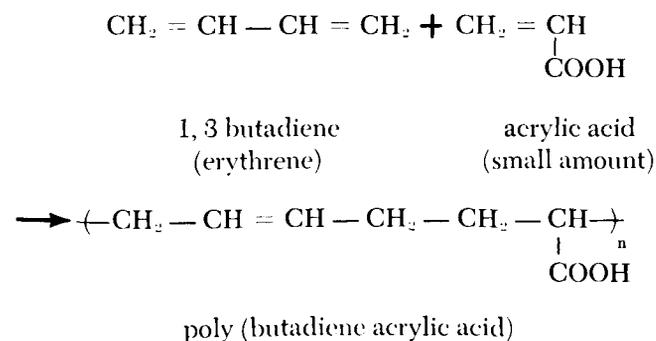
¹The commercial product has approximately 8% monofunctionality.
²Other impurities, side reactions, different reaction rates, and other unknown factors contribute also to the necessity of excess of TDI.

strength, but also in high sensitivity of the formulation to the stoichiometric balance of the isocyanate and hydroxyl groups (Ref. 9).

The usual oxidizer and light metal as fuel additives in the polyurethane solid propellant are ammonium perchlorate and aluminum powder. Castable solid grains for gas generator devices requiring gases of low temperature do not use any light metal fuel (which increases the combustion temperature). The gas generator grains use ammonium nitrate as the oxidizer (usually below 80%) stabilized with squalene (C₃₀H₅₀) (Ref. 10), which is an unsaturated hydrocarbon and acts as a plasticizer and nitric acid scavenger. Previously, ammonium nitrate could not be used in polyurethane propellants because traces of free nitric acid were always present in the oxidizer. These traces autocatalytically formed more nitric acid (and ammonia) which degraded the urethane linkages.

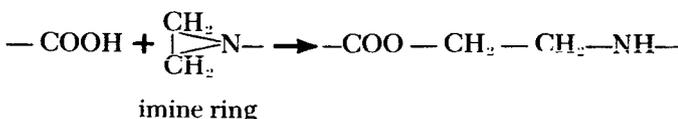
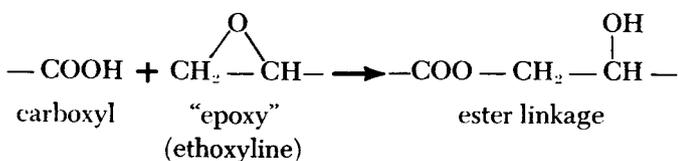
B. PBAA Propellant

The development of a solid propellant using a binder based on a copolymer of polybutadiene and acrylic acid (PBAA) began about 5 yr ago. The advantage of this propellant was in the higher solid loading (Ref. 5) (over 85%) which resulted in a higher specific impulse. However, a too rapid aging and a shift in critical properties such as modulus and elongation constitute real drawbacks. Since the history of the development of the PBAA propellant is relatively short, the experience in the reactivities of the carboxyl groups (which are randomly distributed), the degree and nature of the cross-links, and their sensitivity to moisture, heat, and aging are not yet fully understood. The copolymer PBAA (prepolymer) is obtained by the following reaction:

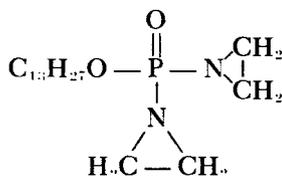


The PBAA copolymer is used as a low viscosity liquid which is mixed with a solid oxidizer, light metals (or their hydrides), and a curing and/or cross-linking liquid agent. These agents may contain either epoxy or imine

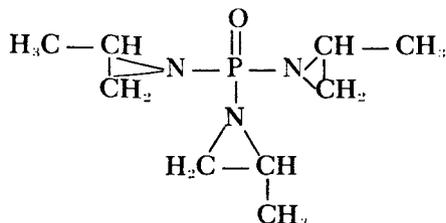
functional groups which react on curing with the carboxyl groups.



Thus, the PBAA binder after curing consists of a copolymer of butadiene and acrylate without or with a nitrogen linkage (from the imine group). The curing and/or cross-linking is carried out by epoxy or imine agents which can be di- or tri-functional (e.g., di- or tri-epoxide). The imine agents are often used in the form of aziridinyl derivatives, i.e., compounds containing ethylene imine group. A typical di-functional aziridine compound is tridecyl diaziridinyl phosphinate



A typical tri-functional aziridine compound is MAPO (a trade name), a highly reactive tri-derivative of phosphorous oxychloride and propylene imine (Ref. 11)



which is tris- [(1-(2-methyl)-aziridinyl) phosphine oxide. MAPO is used quite often as a cross linker in many polymer systems which contain active hydrogen.

PBAA was the first of the "polybutadiene" rubbers used for solid propellant. The others, known as PBAN and CTPB and described below, came later.

C. PBAN Propellant

This type of propellant is based on another "polybutadiene" binder. PBAN is a terpolymer of polybutadiene-, acrylic acid-acrylonitrile. The carboxyl groups in the liquid prepolymer are randomly distributed; they are cured and/or cross-linked with agents as in the case of the PBAA propellant. Polybutadiene-acrylonitrile copolymer without acrylic acid has been used in the preparation of nitrile rubber. PBAN like PBAA propellant usually contains 85% by weight of solid loading and has good physical (mechanical) properties. Both these "polybutadiene" propellants (Ref. 5) are similar in performance over a wide temperature range, wider than that for the polyurethane propellant.

These propellants, however, also pose problems. The main problem is the great sensitivity to small variations of the several ingredients necessary to form the binder. Of prime importance is the proper characterization of the prepolymer, so that the reproducibility of the propellant during processing is achieved. Sensitivity to moisture, storability, thermal stability, vibrational-fatigue resistance, and physical properties are strongly dependent on the proper curing agents, various additives, and processing conditions. Of great concern is the aging of these propellants and a shift in tensile strength, elongation, and modulus. All these difficulties are now being investigated and their causes researched.

D. CTPB (CTPBD) Propellant

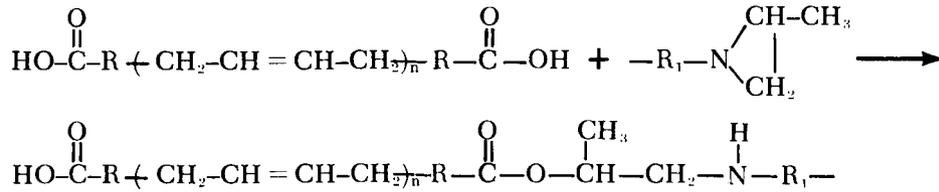
A recent and promising "polybutadiene" binder is the α , ω -carboxyl- (or carboxylic acid, also called carboxy) terminated polybutadiene (CTPB)⁶ (Refs. 12 through 14) which is cured and cross-linked with epoxy or imine agents. The prepolymer is a "tailor-made" liquid of highly regular polymeric structure which can readily be converted into a high molecular weight elastomer with exceptional properties. Characteristics of a typical prepolymer are as follows: color: dark amber; molecular weight: below 4,000; specific gravity: 0.91; viscosity at 120°F: 50 poise and at 80°F: 200 poise; moisture: below 0.1%, and carboxyl equivalent: 0.05/100 g.

The carboxyl groups are in terminal (di-functional) position so that the cured and slightly cross-linked polymer provides a more effective stress distribution than the other low-molecular-weight butadiene polymers. Properties can be controlled by the use of a blend of

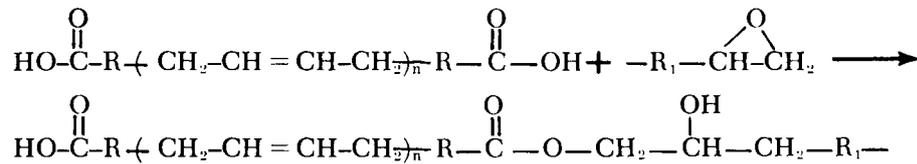
⁶Prepolymers in this class have trade names "Butarez" and "HC Polymer."

di-functional with tri-functional imines or epoxides, combination of imines and epoxides, or through addition of plasticizers. The chemical reactions are as follows:

With imines:



With epoxides:



The cured polymer is used not only as a binder for solid propellant but also as a liner for bonding the cast propellant grain to the rocket case. Asbestos fibers ("floats") are often used as additives in the liner formulation. Good shear adhesion to the steel case is obtained, at temperatures up to 200°F even after extended periods of aging. A typical liner formulation in weight percent is: CTPB pre-polymer 84.20%, MAPO (see PBAA propellant) 2.22%, a tri-functional epoxide 1.78%, asbestos floats (a filler) 10.30%, iron octasol (a catalyst) 0.50%, and "Thixcin" (an additive to make the compound thixotropic and allow the liner to be applied to one coat) 1.00%. Typical cured physical properties of such liners when measured at 80°F, are (Ref. 14):

Tensile strength	250 psi
Ultimate elongation	210 in./in.
Shore hardness A	50
Coefficient of thermal expansion	120 × 10 ⁶ in./in.°F.
Thermal conductivity	5 × 10 ⁴ cal/cm-sec-°F
Specific heat	0.44 Btu/lb-°F
Density	0.99

IV. FUTURE SOLID PROPELLANTS

Solid propellants for future use in space missions must offer higher performance, and at the same time withstand the special environmental conditions imposed by such missions. These conditions include long-term storage in transient and sterilization by heat in advance of launch (for cases as explained on p. 11). The higher performance will be obtained by the use of more energetic oxidizers and/or fuels, whereas the other improved characteristics will come from the use of specially developed binders. The advanced solid propellant will yield a high heat release in the chamber while generating low molecular

weight gases. The latter requirement is rarely satisfied due to the presence of H₂O, CO₂, CO, HCl, and N₂ in the exhaust gases from the nozzle; additionally solid propellant containing metals as elements, hydrides, or as part of the oxidizer produce, in the exhaust gases, condensed metal oxides which further lower the performance. Although the presence of light metals and their hydrides increases the chamber temperature which is beneficial, it is also detrimental because it causes a "two-phase" flow (discussed further) and some dissociation of gases (including hydrogen molecules into atoms). The dissociation of gases

absorbs energy instead of changing it into the directed kinetic energy of the exit gases (especially for small expansion ratios).

A. Advanced Solid Oxidizers and Fuels

Oxidizers used in composite propellants are inorganic compounds (although some organic compounds have been suggested). These compounds possess a stoichiometric excess of oxygen which is used to oxidize the binder-fuel and the solid fuel additives, i.e., light metals and/or their hydrides.

Metal atoms, if present in the oxidizer molecule and in solid fuel additives, will cause an undesirable two-phase or three-phase flow in the rocket nozzle due to the presence of liquid or solid combustion or decomposition products, which are suspended in the combustion gases as tiny particles. The present oxidizers avoid the use of metal atoms in their molecules, thus achieving a higher specific impulse of the propellant. On the other hand, presence of solid fuel additives is necessary to further increase the specific impulse, as heat released on combustion of these additives greatly increases the temperature in the rocket chamber (to 6,000°F and beyond).

The reasons for the undesirability of the presence of solid and/or liquid particles in the combustion gases are numerous (Ref. 15):

1. The volume of each of these particles is negligible in comparison with the volume of the rocket exhaust gases of the same weight. Thus, the solid/liquid particles do not contribute to the theoretical effective and characteristic exhaust velocities (c , c^*) nor to the theoretical specific impulse (only during combustion, but not afterward). Although the free metals or their hydrides have an extremely attractive heat release, the performance (I_s delivered) is reduced by 5% and cannot be greater than 92% (Ref. 16).
2. Great losses result from thermal and velocity lags between the hot solid/liquid particles and expanding gases.
3. The two-phase or three-phase flow contributes to the erosion.

Table 3 (an adaptation from Ref. 17, p. 356) shows different oxidizers and their available oxygen to oxidize the molecules or atoms of fuel-binder and solid-fuel additives.

Table 3. Oxidizers ranked by oxygen content

Formula	Name	Available oxygen, wt %	Specific gravity	Development status and (Remarks)
Solid O ₂	Frozen oxygen	100		(Cryogenic)
LiO ₃	Lithium ozonide	73		Distant future
NO ₂ ClO ₄	Nitronium perchlorate or nityl perchlorate	66	2.22	(Very hygroscopic, Refs. 16 and 18)
LiO ₂	Lithium superoxide	61		Future
LiClO ₄	Lithium perchlorate	60	2.43	(Very hygroscopic)
Mg(ClO ₄) ₂	Magnesium perchlorate	57	2.60	(Very hygroscopic)
LiNO ₃	Lithium nitrate	58	2.38	(Hygroscopic)
NaO ₃	Sodium ozonide	56		Future
H ₃ OClO ₄	Oxonium perchlorate or perchloric acid, 84.8%	54	1.88	(Hygroscopic; melts at 122°F)
Ca(ClO ₄) ₂	Calcium perchlorate	54		(Not attractive)
NaClO ₄	Sodium perchlorate	52		(Hygroscopic)
Solid H ₂ O ₂	Hydrogen peroxide	47	1.71	Future
KClO ₄	Potassium perchlorate	46	2.52	Was used
KO ₃	Potassium ozonide	46		(Not attractive)
Ca(O ₂) ₂	Calcium superoxide	46		(Not attractive)
NaO ₂	Sodium superoxide	44		(Not attractive)
NaClO ₃	Sodium chlorate	45	2.49	(Not attractive)
NH ₂ OH.HClO ₄	Hydroxyl amine perchlorate	42		Was used (Ref. 19)
H ₂ H ₆ (ClO ₄) ₂	Hydrazine (hydrazinium) dperchlorate	41	2.2	(Hygroscopic, Ref. 20)
KNO ₃	Potassium nitrate	40	2.1	(Not attractive)
NH ₄ ClO ₄	Ammonium perchlorate	34	1.95	Widely used
H ₂ H ₆ ClO ₄	Hydrazine perchlorate	24		(Detonable, Ref. 21)
NH ₄ NO ₃	Ammonium nitrate	20	1.73	In gas generators
N ₂ H ₃ NO ₃	Hydrazine nitrate	8.4		(Melts at 159°F; sublimes at 284°F)
C ₃ H ₅ (NO ₃) ₃	Nitroglycerine	3.5	1.59	(Melts at 56°F)

The available oxygen is that which has not been consumed during combustion by the atoms within the oxidizer molecule. Thus, $KClO_4$ has four oxygen atoms available, but $NaNO_3$ has only $2\frac{1}{2}$ oxygen atoms available as some of the oxygen is used up to form $\frac{1}{2}Na_2O$. NH_4ClO_4 has only $2\frac{1}{2}$ oxygen atoms (34% by weight) available because of the decomposition reaction (in which trace formation of nitrogen oxides were neglected):



Oxidation of atoms within the molecule of oxidizer is a monopropellant reaction; formation of gaseous products during such reaction (especially the ones with a low molecular weight like H_2O , HF , etc.) give a high volume per pound, and hence are beneficial to rocket performance as opposed to the solid or liquid products of the reaction, i.e., the solid or liquid metal oxides or chlorides.

In the selection of solid oxidizers for propellants, it is important to consider:

1. Highest possible heat of formation (ΔH_f).
2. Availability of oxygen.
3. Monopropellant action.
4. High thermal stability, i.e., a high decomposition temperature.
5. Compatibility with the binder and fuel additives during processing and storage.
6. Density (which should be as high as possible).
7. Ease in obtaining the desired particle size (bi- or tri-modal distribution in order to obtain the highest sedimentation volume and best packing in the propellant with a minimum of binder).
8. Hygroscopicity which sometimes requires a very dry processing room atmosphere.
9. Low sensitivity to impact and friction.
10. Phase changes during processing, storage, and temperature cycling (e.g., NH_4NO_3 undergoes crystalline phase changes at 1, 90, and 184°F which result in volume changes and may cause difficulties).
11. Purity (especially no traces of water or free acids).
12. Availability and cost.
13. Ease in transportation.

All the foregoing considerations, with the exception of the first three, apply to the solid fuel additives as well. At any time Be or its compound is used as the solid fuel additive, toxicity of the rocket exhaust or from an inadvertent explosion during processing or storage must also be taken into consideration.

The theoretical performance of pure light-element hydrides with different solid oxidizers is given in Refs. 22 and 23; Table 4 shows these performances. However, specific impulse of solid propellants which contain polymeric binder necessary to bind the non-cryogenic oxidizer with metal hydrides will be lower than in Table 4. The delivered specific impulse will be lowered even further.

**Table 4. Theoretical maximum specific impulse at shifting equilibrium (Refs. 22 and 23).
 $P_c = 1,000$ psia, $P_e = 0.2$ psia**

Fuel	Oxidizer	Oxidizer, wt %	I_p , sec	T_c , °K
B_5H_9 (frozen) ^a	H_2O_2 (frozen)	73	<399	<3400
	O_2 (frozen)	72	<421	<4620
	NO_2ClO_4	79	389	4502
	NH_4ClO_4	73	370	3000
MgH_2	H_2O_2 (frozen)	42	<368	<3073
	O_2 (frozen)	33	<357	<3216
	NH_4ClO_4	53	348	3080
	NO_2ClO_4	43	346	3288
AlH_3	H_2O_2 (frozen)	48	<424	<3923
	O_2 (frozen)	44	<416	<4374
	NH_4ClO_4	58	393	3837
	NO_2ClO_4	51	397	4252
BeH_2	H_2O_2 (frozen)	61	<498	<3884
	O_2 (frozen)	53	<492	<4004
	NH_4ClO_4	62	446	3283
	NO_2ClO_4	64	456	4132
LiH	H_2O_2 (frozen)	81	<341	<2711
	O_2 (frozen)	66	<342	<3309
	NH_4ClO_4	63.5	326	2292
	NO_2ClO_4	73	333	3292

^aFrozen propellants are explained in Sect. IV-C.

Figure 1 (taken from Ref. 24) shows the theoretical standard I_s of different solid propellants composed of ammonium perchlorate, light metals, and binder. The highest I_s is 290 sec for the Li-Be curve. The vacuum I_s would then be well over 300 sec. It is the judgment of the author that, in the near future, (noncryogenic) solid propellants will be developed for space application with a delivered vacuum I_s between 300 and 350 lbf-sec/lbm which, for these applications, would be competitive with liquid propellants.

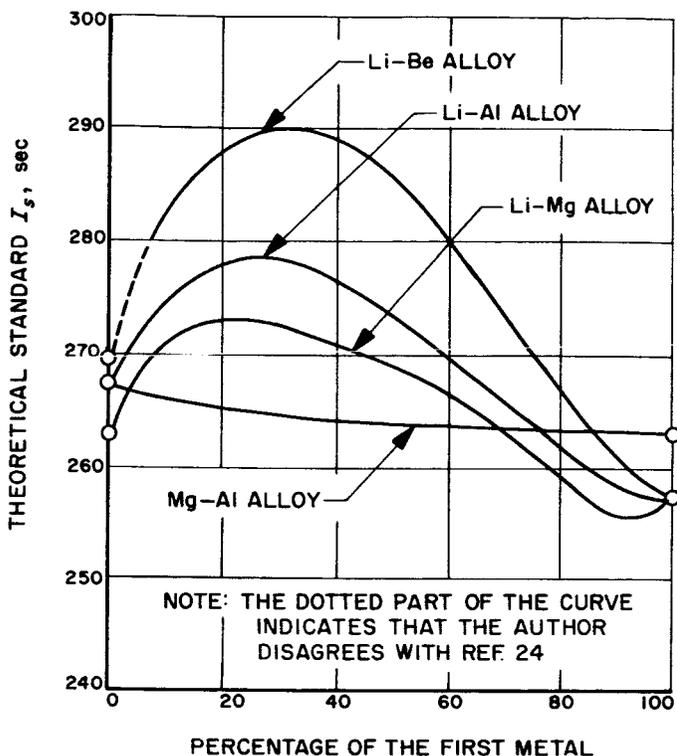


Fig. 1. I_s versus alloy composition in polyurethane propellants (NH_4ClO_4 and alloy content are at optimum, Ref. 24)

B. Advanced Propellant Binders

Various attempts are being made to obtain polymeric binders which will be suitable for advanced solid rockets needed in space missions. The special characteristics required for such applications are many. Some are described in the following paragraphs.

Such binders should be compatible with high-energy ingredients and permit, at the same time, a high solids loading. It should be non- (or minimally) hygroscopic, reproducible, have good physical properties (also after long storage and temperature cycling), and be preferably nontoxic. For easy mixing binder components should possess a relatively narrow molecular-weight distribution. This property, as well as low molecular weight, results in a pre-polymer of low viscosity. High molecular-weight species influence the viscosity of the pre-polymer more than the low ones; thus, a polymer having a narrow molecular-weight distribution has a lower viscosity for a given average molecular weight.

The heat of formation (ΔH_f) of the binder should be as high as possible to achieve high specific impulse. For this purpose, the solid oxidizer should have a high per-

centage of available oxygen and the ΔH_f also as high as possible (both ΔH_f should be least negative or preferably positive).

Further, the binder should produce a propellant which on burning will not attenuate radio microwave (radar) used for radio guidance and telecommunication (telemetry and voice communication) such as high frequency (3 to 30 Mc), very high frequency (30 to 300 Mc), and microwaves (1,000 to 6,000 Mc). Attenuation is caused by the presence of an excessive number of electrons in the exhaust attributable to high temperature.

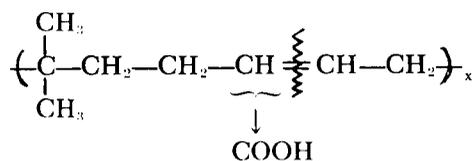
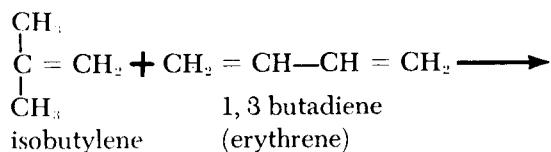
The binder should be suitable for sterilizable solid propellants (Ref. 25) needed for spacecraft landing missions on the surfaces of Mars, Venus, Mercury, Jupiter, etc. The sterilization is required to prevent any possible contamination of these planets with Earth organisms that may affect their ecology. The sterilization of the landing portion of planetary spacecraft will be carried out by heat. The propellant must therefore withstand three 36-hr cycles of heating to 145°C (293°F) and retain very high reliability. The coefficients of thermal expansion of the propellant and of the steel casing should be as close as possible in order to prevent high compressive stresses, buckling, cracking of the grain, and breaking the bond between the propellant, liner, and case.

In order to withstand low temperatures to which the propellant may be exposed in space, the binder should possess a low glass transition temperature. It should exhibit only a negligible vaporization loss in the hard vacuum of space during extended space missions and be resistant to nuclear radiation of energetic protons, electrons, and gamma rays which originate in solar events (solar flares causing solar storms) and/or in nuclear devices (reactors or radioactive isotopes) carried aboard a spacecraft.

Fluorinated binders have been suggested for high-energy acidic oxidizers because of their excellent compatibility (Ref. 26). Fluorinated binders have a greater density than hydrocarbon binders and can withstand high temperature; hence, they may be used in the fabrication of heat-sterilized solid propellant. However, presence of carbon-bonded fluorine in the binder-fuel molecule is undesirable because it decreases energy in this state. Fluorinated polymers that have been considered for solid propellant binders, basically have formulae of the type $\text{CH}_2\text{F}_n\text{O}_2$. Fluoro-olefins studied include perfluorocumulenes, tetrafluoroallene, monofluoroacetylene, perfluorobutadiene, etc.

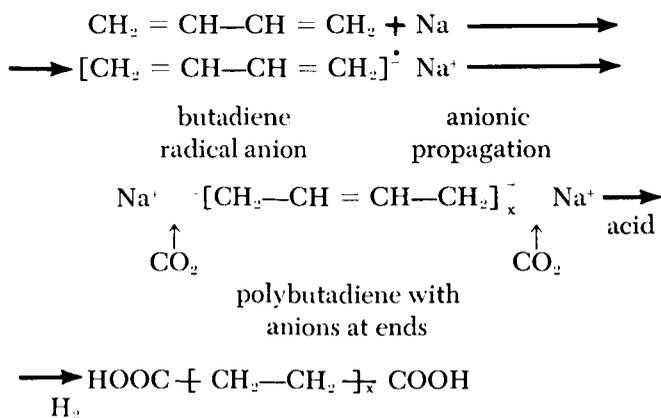
Fully or partially saturated polymeric binders have also been suggested. The following methods are being tried to prepare the appropriate prepolymers.

1. Copolymerization of isobutylene and butadiene using cationic polymerization catalysts (which are Friedel-Crafts catalysts such as $AlCl_3$, BF_3 , and other strong Lewis acids) leads to Butyl A rubber (Ref. 27). The rubber is then cleaved (degraded) by a controlled oxidation to form carboxyl terminated polyisobutylene liquid pre-polymer which is then cured (cross-linked) in the usual manner:



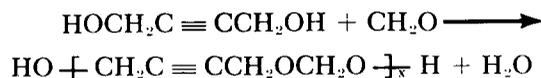
carboxyl terminated polyisobutylene

2. Polymerization of butadiene by use of a "living polymer" technique with catalyst such as metallic sodium provides good control of the molecular weight and molecular weight distribution (Refs. 13 and 28). This is an anionic polymerization which is terminated by the introduction of CO_2 (or H_2O) followed by acidification to form carboxyl or (hydroxyl) groups at the end of the linear polymer:



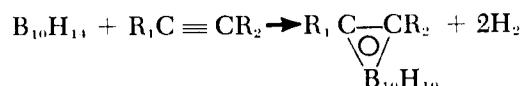
Other binders which have been suggested but so far found of little use are as follows. A high-energy binder

was prepared from acetylenic monomer (Ref. 29) butyne-diol and formaldehyde and used for a castable solid propellant:



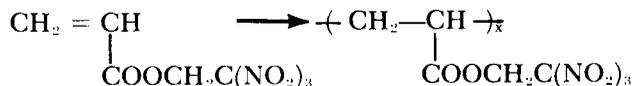
Presence of the triple (alkyne) bond increases the energy of formation of the binder.

Efforts have been made to incorporate boron hydrides into polymer systems (Ref. 12). A major development consisted of the discovery of carboranes which were extremely stable and organophilic. They are synthesized from decaborane and alkynes:



It was also possible to prepare hydroxyl- and carboxyl-terminated prepolymer which on curing and cross-linking yielded a resilient rubbery product.

Various attempts have been made to reduce the solid oxidizer loading by incorporating oxygen in the form of the nitro and nitrate groups into the polymeric structure (Ref. 12). The nitrate systems were found to be thermally unstable contrary to the nitro polymers which are obtained either by addition or condensation polymerization:



C. "Cold" and Cryogenic Solid Propellant

Cryogenic solid propellant (Ref. 26) could be prepared by dispersing one of the hydrides in liquid oxygen, pouring the mixture into a rocket chamber, and cooling to a temperature below $-361^\circ F$, i.e., below the solidification of liquid oxygen. The cooling and storage of such propellant could be accomplished by keeping the rocket in liquid hydrogen, which boils at $-422^\circ F$. Because there will be a two-phase flow of gases and solid and/or liquid particles of light metal oxides, the expected delivered I_s would be considerably less than the theoretical specific impulse.

A mixture of solid oxygen and hydrogen will exist below $-434^\circ F$. Such mixture is not hypergolic; it could be made by pouring liquid oxygen into liquid hydrogen dur-

ing cooling (e.g., by adiabatic evaporation of liquid hydrogen). A mixture composed of powdered beryllium and frozen oxygen and hydrogen will give a theoretical standard I_s of 455 and vacuum 540 lbf-sec/lbm (similar to the non-frozen triplex system in tribrid, as in U.S. Patent 3,112,009, December 1963).

"Cold" solid propellants could be made by mixing frozen H_2O_2 or liquid H_2O_2 and freezing later (freezing point + 30°F) with light metals such as aluminum or lithium or their hydrides. Table 4 shows that the theoretical vacuum specific impulse with beryllium hydride

will then reach 498 lbf-sec/lbm.

"Cold" solid propellants may be made by freezing a liquid monopropellant (e.g., nitromethane or hydrazine), a homogenized mixture of non-hypergolic bipropellants (e.g., RP-1 with N_2O_4), a homogenized mixture of a liquid oxidizer and powdered fuel, or a high-energy solid propellant mix which is unstable at ordinary temperature but stable at low temperature. Such propellants may even be made space-storable by providing a proper insulation, heat conductive outer shell, and proper paint on that shell. Successful development of all "cold" and cryogenic solid propellants belongs to the future.

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